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Atmospheric emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate

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[1] The fate of deepwater releases of gas and oil mixtures is initially determined by solubility and volatility of individual hydrocarbon species; these attributes determine partitioning between air and water. Quantifying this partitioning is necessary to constrain simulations of gas and oil transport, to predict marine bioavailability of different fractions of the gas-oil mixture, and to develop a comprehensive picture of the fate of leaked hydrocarbons in the marine environment. Analysis of airborne atmospheric data shows massive amounts (~258,000 kg/day) of hydrocarbons evaporating promptly from the Deepwater Horizon spill; these data collected during two research flights constrain air-water partitioning, thus bioavailability and fate, of the leaked fluid. This analysis quantifies the fraction of surfacing hydrocarbons that dissolves in the water column (~33% by mass), the fraction that does not dissolve, and the fraction that evaporates promptly after surfacing (~14% by mass). We do not quantify the leaked fraction lacking a surface expression; therefore, calculation of atmospheric mass fluxes provides a lower limit to the total hydrocarbon leak rate of 32,600 to 47,700 barrels of fluid per day, depending on reservoir fluid composition information. This study demonstrates a new approach for rapid-response airborne assessment of future oil spills. **Citation:** Ryerson, T. B., et al. (2011), Atmospheric emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate, *Geophys. Res. Lett.*, 38, L07803, doi:10.1029/2011GL046726.

1. Introduction

[2] A fatal explosion and fire on April 20 during drilling operations at the BP Macondo wellhead, 80 km offshore in 1520 m of water in the Gulf of Mexico, led to the loss of the Deepwater Horizon (DWH) oil platform. The ensuing leak

lasted over three months and spilled millions of gallons of oil into Gulf waters [Crone and Tolstoy, 2010]. The majority of DWH response efforts have focused on determining hydrocarbon leak rate [Crone and Tolstoy, 2010], dispersion [Adcroft et al., 2010; Mezić et al., 2010], and ecosystem impacts [Camilli et al., 2010; Diercks et al., 2010; Graham et al., 2010; Hazen et al., 2010; Kessler et al., 2011; Valentine et al., 2010] based on measurements made in the water column.

[3] DWH emissions were not confined to the water column. A significant, but previously undefined, fraction of leaked hydrocarbon mass at the ocean surface evaporated [National Research Council, 2003], resulting in emission of a wide range of volatile organic carbon (VOC) compounds to the atmosphere. Spill remediation efforts, such as deliberate burning of surface oil and flaring of gas separated from recovered oil, represent additional sources of combustion products to the atmosphere. The transport and dispersion of oil-related carbon compounds from a major, deepwater marine blowout of natural gas and liquid oil is not well characterized, as most previous marine spills have occurred at the surface (e.g., liquid oil from *Exxon Valdez* and *Amoco Cadiz*) or in shallow water (e.g., natural gas and liquid oil from the 1969 Santa Barbara blowout [Foster et al., 1971] and from *Ixtoc I* [Jernelöv and Lindén, 1981]).

[4] In this study we present airborne *in situ* measurements (publicly available at esrl.noaa.gov/csd/tropchem/2010gulf/) of DWH emissions taken from an instrumented P-3 research aircraft showing massive amounts (exceeding 258,000 kg/day) of spill-related hydrocarbons evaporating promptly to the atmosphere. These flights took place during initial containment and cleanup operations, several days after the damaged riser from the blowout preventer had been removed and a cap (Top Hat #4) had been loosely secured over the wellhead. We use the atmospheric data to quantify primary emissions from (i) evaporation of surface oil that had escaped the cap and had risen through the water column, and (ii) flaring of natural gas recovered via the cap (Figure 1). Emissions from deliberate burning of surfaced oil were measured but are not presented here.

2. Air-Water Partitioning of Surfaced Reservoir Fluid

2.1. Dissolution of Methane and Light Hydrocarbons

[5] Hydrocarbon vapor pressure increases with decreasing carbon number; thus, methane (CH₄) and the lightest VOCs

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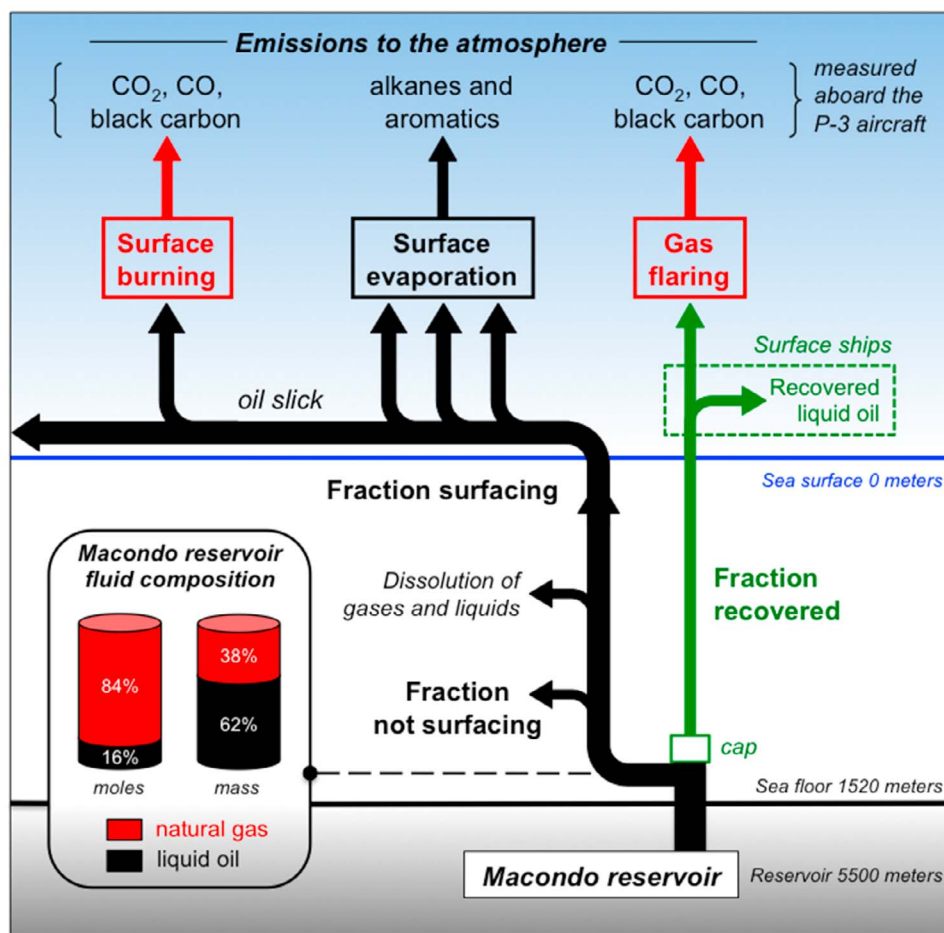


Figure 1. Schematic of oil carbon and combustion product partitioning in the marine environment. Airborne *in situ* measurements quantify mass flux along each of the three atmospheric emissions pathways shown; drawing is not to scale. The fraction surfacing can be altered by dissolution in the water column, but has a significant surface expression. In contrast, the fraction not surfacing is that reservoir fluid (gas plus oil) presumably emitted in droplets with insufficient buoyancy to reach the surface, and thus has no surface expression.

are expected to evaporate rapidly and completely upon reaching the ocean surface [Fingas, 1999]. CH_4 accounts for 65% of the molecules (20% of the mass) in the leaking reservoir fluid (details in the auxiliary material; Table S4). Atmospheric abundance of CH_4 was measured continuously with a precision of ± 1.5 parts per billion by volume (ppbv) at ~ 100 m spatial resolution along the aircraft flight tracks. No CH_4 enhancements correlated with the spill were detected on either of the two P-3 survey flights (e.g., Figure S1); rather, CH_4 variability is attributed to larger-scale atmospheric transport and mixing of air masses affected by sinks and sources unrelated to the spill. Subsurface measurements of DWH CH_4 [Camilli *et al.*, 2010; Valentine *et al.*, 2010] document large enhancements with maxima at depths below 800 m but do not quantify its fraction; the atmospheric data from shipborne [Kessler *et al.*, 2011; Yvon-Lewis *et al.*, 2011] and P-3 airborne measurements demonstrate essentially complete dissolution of CH_4 , substantiating an early prediction [Valentine, 2010] on CH_4 fate in the subsurface water column.

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GL046726.

[6] Ethane (C_2H_6) and benzene (C_6H_6) from evaporation of surfaced oil were positively detected, but with peak enhancements of less than 250 and 50 parts per trillion by volume (pptv), respectively. Minimal enhancement of C_2H_6 and C_6H_6 in the atmosphere, despite their presence in substantial amounts in the reservoir fluid (Table S4), demonstrates nearly complete dissolution of these VOCs in the water column prior to surfacing. The atmospheric data further demonstrate partial, compound-specific removal of heavier alkanes from C_3 through isomers of C_6 , and light aromatics from C_6 through C_9 , likely determined by their relative solubility in seawater [Shaw *et al.*, 2006]. These species are shown in Figure 2 with fractions in air (atmospheric enhancement relative to abundance in the reservoir fluid, normalized to *n*-heptane) between 0 and 1.

[7] The air-water partitioning shown in Figure 2 defines the speciation and relative abundance of leaked hydrocarbons that remain dissolved in the water. The airborne data also define the range of hydrocarbons for which dissolution of significant mass from the surfacing fraction appears to be negligible. This provides a rigorous constraint on surface and subsurface plume simulations [Adcroft *et al.*, 2010; Mezić *et al.*, 2010], which should successfully predict

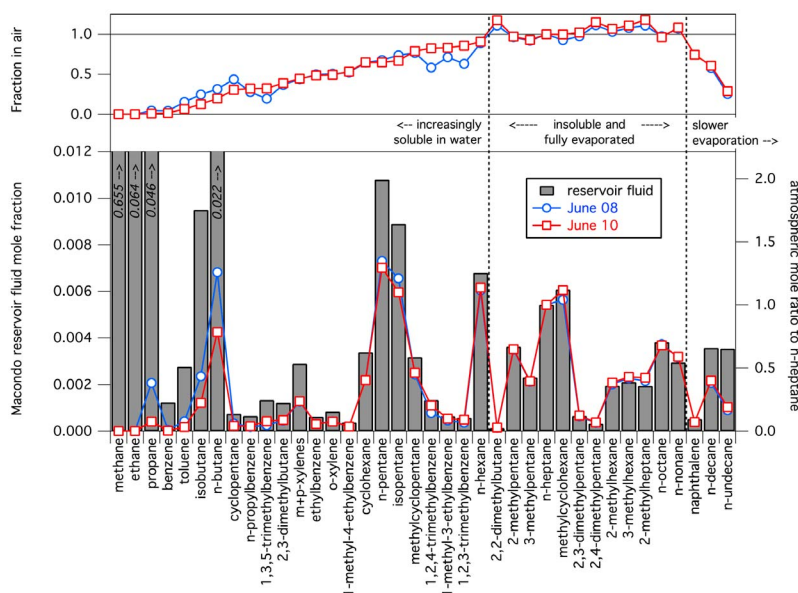


Figure 2. Atmospheric plume enhancement ratios, relative to *n*-heptane, of VOC species for June 8 (blue circles) and June 10 (red squares) reflect the composition of the Macondo reservoir fluid (black bars). The fraction in air is the atmospheric enhancement ratio normalized to the expected ratio to *n*-heptane in the reservoir fluid.

air-water partitioning of surfacing hydrocarbons commensurate with the above observations.

[8] Multiplying the derived fractions in air by reservoir fluid mass fractions shows that under the steady-state conditions of June 10, ~33% of the surfacing hydrocarbon mass dissolved in the water column; the balance of the fraction surfacing, ~67%, did not dissolve to a significant degree. These values can evolve over time, as dilution in water over days to weeks will dissolve additional mass of even sparingly soluble species; however, other removal processes (evaporation, biodegradation, and surface burning) will compete with dissolution on these time scales. Different aquatic bioavailabilities are therefore predicted for the dissolved and undissolved fractions of leaked hydrocarbons, due to their different physical-chemical states and distributions in the marine environment.

2.2. Prompt Evaporation of Volatile Hydrocarbons

[9] Leaked hydrocarbons that do not dissolve completely can evaporate after reaching the surface. Substantial atmospheric enhancements due to evaporation, some exceeding tens of ppbv, for C_2 through C_{11} hydrocarbons were observed on both flights in narrow plumes (~2 km wide at 10 km distance) extending downwind of the DWH spill site (Figure S1). No enhancements above background variability of these species (tens of pptv) were detected 10 km upwind of DWH, positively identifying the incident site as the source of the observed VOC plumes. The atmospheric plume VOC composition sampled on both flights (Figure 2) corresponds to that of the leaking reservoir fluid modified by partial or complete removal of soluble species in the water column.

[10] Observed enhancements represent 100- to 1000-fold increases of VOC species above their background mixing ratios; they demonstrate prompt evaporation of the most volatile hydrocarbons from a relatively small area (upper limit of ~2 km²) of freshly surfaced oil. The prompt time-

scale of roughly 2–3 hours is determined by evaporation rates [Fingas, 1999] for the range of VOCs measured aboard the aircraft. Slower evaporation of hydrocarbons $\geq C_{10}$ likely contributes to plume spreading [de Gouw *et al.*, 2011] and thus smaller derived atmospheric abundances for these less volatile species (Figure 2). Multiplying the fractions in air by the respective reservoir fluid mass fractions shows that under the steady-state conditions of June 10, ~14% of the surfacing hydrocarbon mass evaporated promptly to the atmosphere.

[11] Atmospheric enhancement ratios ($\Delta X_i/\Delta(n\text{-heptane})$) identical to ratios in the Macondo reservoir fluid (Table S4) were observed for a subset of light alkane isomers from 2,2-dimethylbutane through *n*-nonane (Figure 2). Solubility in seawater for this range of compounds, while low, varies by a factor of 20 [Shaw *et al.*, 2006], ruling out equal but nonzero dissolution for this range of hydrocarbons. We conclude the hydrocarbons in Figure 2 with a fraction in air approaching unity (isomers of C_6 through *n*- C_9) represent a subset of the escaped fluid that transited the water column with negligible dissolution and evaporated completely within hours of reaching the surface [Fingas, 1999]. This subset is used to calculate the surfacing rate of leaking hydrocarbons, as discussed below.

3. Atmospheric Hydrocarbon Mass Fluxes

[12] We use standard methods [Ryerson *et al.*, 1998, 2001; Trainer *et al.*, 1995; White *et al.*, 1976] to quantify atmospheric VOC mass fluxes from evaporation of surfaced oil on June 10 (Figures S1b, S1d, and S1f). Fluxes are calculated (details in auxiliary material) at each crosswind transect for all VOC species measured aboard the aircraft (Tables S2 and S3); these values are extrapolated to daily fluxes from the plume transect data taken over the course of 4 hours. Analysis of nine independent transects of the plume

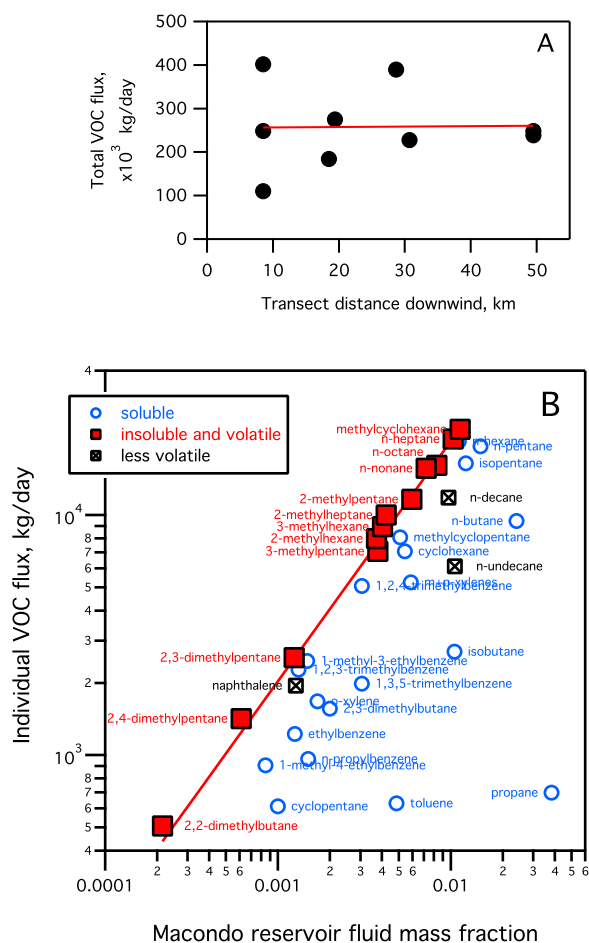


Figure 3. (a) Atmospheric mass flux of all measured VOCs evaporating from the fresh oil slick on June 10 as a function of distance downwind of the DWH incident site. (b) Atmospheric mass fluxes of individual VOCs on June 10, 2010 for soluble (blue), insoluble and volatile (red) and less volatile (black) compounds as a function of the Macondo reservoir fluid mass fraction. Benzene, ethane, and methane data are off scale due to negligible or zero atmospheric flux.

gave an average of 258,000 kg/day of hydrocarbons evaporating promptly from the fresh oil slick on June 10 (Figure 3a); the measured sum of C_6 through C_{11} aromatic compounds contributed 45,000 kg/day to this amount.

[13] The prompt flux of volatile hydrocarbons does not include mass from slower evaporation of semi-volatile compounds [de Gouw *et al.*, 2011; Fingas, 1999], which were not measured directly in this study. However, organic aerosol mass measurements aboard the aircraft suggest an additional $\sim 200,000$ kg of hydrocarbons $>C_{11}$ were evaporating over 10–100 hour time scales after surfacing [de Gouw *et al.*, 2011], substantially increasing the calculated mass removed from the water. Uncertainties [Ryerson *et al.*, 1998; Trainer *et al.*, 1995] of $\pm 50\%$ in the atmospheric VOC flux are dominated by assumptions of vertical mixing in the atmosphere and, to a lesser extent, by the calculation of plume integrals from the discontinuous VOC data (details in auxiliary material).

3.1. Evaporative Emissions Constrain the Surfacing Flow Rate

[14] The insoluble and volatile subset of surfacing DWH hydrocarbons consists of compounds with atmospheric fractions approaching unity in Figure 2. Since these compounds are transported to the surface without differential loss and evaporate promptly, atmospheric VOC mass fluxes coupled with reservoir fluid composition data (Table S4) provide an independent means to calculate the surfacing rate of leaked reservoir fluid. The calculation is possible using the atmospheric flux of any single species [White *et al.*, 1976] surfacing without differential loss, and should be identical across the range of species chosen.

[15] The calculated atmospheric mass fluxes of the insoluble and volatile subset are linearly related and highly correlated ($r^2 = 0.992$) to their respective weight fraction in the original Macondo reservoir fluid (Figure 3b). The slope of this linear relationship gives the surfacing rate directly; the fitted slope of $(2.03 \pm 0.07) \times 10^6$ kg/day (red line in Figure 3b) corresponds to a leak rate of 15,100 barrels of reservoir fluid per day escaping into the water and surfacing on June 10 (details in auxiliary material). Integration of the atmospheric VOC data carries uncertainties of $\pm 50\%$, as noted previously. We separately assign a probable range of -0 to $+100\%$ to this rate due to uncertainties in reservoir composition, arising from unspecified treatment of unresolved heavy VOC species in the chromatographic analyses provided by BP. The probable range for this rate is then 15,100 to 30,200 barrels of reservoir fluid per day escaping the cap and surfacing promptly. This analysis of airborne data provides the only quantified assessment of leaked DWH fluid surfacing flow rates, and provides additional rigorous constraints for numerical simulations of this process.

3.2. Flare CO_2 Emissions Constrain the Fluid Recovery Rate to Surface Ships

[16] In a remediation effort unique to this spill, after June 3 some fraction of the reservoir fluid was recovered via the cap directly to surface ships. Following depressurization and separation of volatile gases, the liquid oil fraction was transferred to a tanker; the gas fraction was then continuously burned in a combustion flare aboard the *Enterprise* recovery vessel (Figure 1). The amount of natural gas flared, and thus the flow rate of reservoir fluid recovered directly, is determined below using flare CO_2 plume measurements on June 10 and flared gas composition data (Table S5).

[17] An *Enterprise* flare emission rate of $(1.3 \pm 0.5) \times 10^6$ kg CO_2 /day is estimated (details in auxiliary material) by calculating the atmospheric mass flux [White *et al.*, 1976] from CO_2 plume enhancement data taken on four crosswind transects performed over the course of 45 minutes. This corresponds to $(6.3 \pm 2.2) \times 10^5$ m³ at standard temperature and pressure (STP) of natural gas recovered, separated from the liquid oil, and flared on June 10. Incorporating gas-to-oil ratio data measured aboard the *Enterprise* on June 10 (www.energy.gov/open/oilspilldata.htm), we find the total recovery rate to surface ships via the cap was 17,500 barrels of reservoir fluid per day based on the atmospheric plume CO_2 flux data on June 10. We note an estimated uncertainty of $\pm 50\%$ in the fluid recovery rate derived from the atmospheric plume CO_2 flux. The derived value is slightly lower than, but within error limits of, *Enterprise* recovery rates

reported on June 10 (www.energy.gov/open/oilspilldata.htm). To our knowledge, the calculation using atmospheric CO₂ fluxes provides the only independent assessment of gas and oil volumes recovered directly to surface ships via the cap for the entire DWH incident response.

3.3. Lower Limit to the Total Fluid Leak Rate

[18] Summing the flows of escaped fluid reaching the surface and fluid recovered to the surface via the cap, we derive a conservative lower limit of 32,600 (range 32,600 to 47,700) total barrels of reservoir fluid per day leaking from the damaged wellhead on June 10. The atmospheric data do not account for any separate fraction of reservoir fluid lacking a surface expression (“fraction not surfacing” in Figure 1) [Diercks *et al.*, 2010; Valentine *et al.*, 2010; Yvon-Lewis *et al.*, 2011]; thus, this analysis provides a robust lower limit to the total flow rate. Estimates based on analysis of subsurface video of escaping gas and oil by academic researchers [Crone and Tolstoy, 2010] and by Federal agencies [U.S. Geological Survey, 2010] suggest a total flow rate of ~60,000 (range 52,000 to 68,000) barrels per day emerging from the wellhead. Additional data quantifying the fraction of reservoir fluid not surfacing (Figure 1) are needed to better constrain the differences between these estimates.

4. Conclusions and Implications

[19] These airborne data define an inclusive picture of the environmental extent and fate of a broad range of hydrocarbons released in a major subsurface leak. Environmental exposures are specific to individual hydrocarbons and their physical state, whether dissolved, evaporated, or undissolved, and thus depend greatly on initial partitioning by solubility and volatility. For benzene (a known human carcinogen), essentially all of the leaked mass dissolved (Figure 2) and likely remained co-located below 800 m with the similarly soluble CH₄ [Camilli *et al.*, 2010; Diercks *et al.*, 2010; Hazen *et al.*, 2010; Valentine *et al.*, 2010; Yvon-Lewis *et al.*, 2011]. In contrast, C₇–C₉ aromatics (Figure 2) were likely differently distributed through the full vertical extent of the water column, increasing the potential for exposure of mid- and shallow-water marine species to significant concentrations of, e.g., substituted benzenes. Further, naphthalene (listed by the U.S. EPA as a possible human carcinogen) reached the surface without significant loss in the fraction surfacing, and likely evaporated completely on hours-to-days time scales thereafter. We find that negligible naphthalene mass remained in the water from the surfacing fraction, minimizing its availability to marine organisms but maximizing its abundance and effects in the atmosphere. Hydrocarbons ≥C₇ and with very low volatilities remained essentially completely in the water as undissolved, weathered oil in its various forms [NRC, 2003].

[20] The airborne assessment described here has general applicability to quantify air-water partitioning and hydrocarbon leak rates in marine environments. Hydrocarbon solubility and volatility values suggest C₈–C₉ isomers will surface without significant mass loss from depths greater than DWH, and C₆–C₇ isomers will evaporate promptly even for releases into cold surface waters [Fingas, 1999]. This approach should therefore be applicable to marine

releases of gas and oil mixtures at any depth or temperature where surface ice cover is less than 100%; complete ice cover would pose a physical barrier to evaporation. Finally, we note that with a suitably instrumented airborne platform and knowledge of leaking fluid chemical composition, atmospheric measurements can provide a near-real-time assessment of marine gas and oil leak rates at remote locations or for incidents that lack subsurface video imagery [Crone and Tolstoy, 2010].

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